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USE OF THE HYDROGEN-VOLATILE-MATTER RATIO IN OBTAINING THE NET HEATING VALUE OF AMERICAN COALS

BY

A. C. FIELDNER AND W. A. SELVIG

WASHINGTON
GOVERNMENT PRINTING OFFICE
1918

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USE OF THE HYDROGEN-VOLATILE-MATTER RATIO IN OBTAINING THE NET HEATING VALUE OF AMERICAN COALS.

By A. C. FIELDNER and W. A. SELVIG.

INTRODUCTION.

DEFINITION OF "TOTAL" AND "NET" HEAT OF COMBUSTION.

The standard methods of analyzing coal as given by the American Society for Testing Materials [a] state that "the results of determinations of caloric power shall be stated either as 'total' heat of combustion or 'net' heat of combustion." Total heat of combustion is defined as the direct result obtained in the bomb calorimeter with the water vapor in the products of combustion condensed to liquid water at the temperature of the calorimeter—that is, from 20 to 30° C.

Net heat of combustion at 20° C. is defined as the heat developed on complete combustion of a unit weight of fuel with the water in the products of combustion passing off as vapor at 20° C., and is calculated as follows:

$$\text{Net heat of combustion in calories} = \text{total heat of combustion} - \frac{\text{per cent H} \times 9 \times 580}{100}$$

$$\text{Net heat of combustion in B. t. u.} = \text{total heat of combustion} - \frac{\text{per cent H} \times 9 \times 1{,}040}{100}$$

CORRECTION OF LATENT HEAT OF VAPORIZATION IN COMPARING FUELS OF WIDELY DIFFERENT HYDROGEN CONTENT.

In American practice it is customary to report the calorific values of liquid and solid fuels in terms of the total heat of combustion, and as the determination of net heat of combustion involves a hydrogen as well as a calorimetric determination, fuels are usually compared on the basis of total heat of combustion, even though the latent heat of the water vapor is never utilized under commercial conditions. Ordinarily in buying coal on a heat-unit basis the competing coals have practically the same hydrogen content and therefore the correction for the amount of heat lost in the water vapor does not vary much. At times, however, fuels of widely different hydrogen content as, for example, bituminous coal and anthracite or petroleum and

[a] Yearbook for 1915, Am. Soc. Test. Mat., p. 624.

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coke, have to be compared. The hydrogen content and total and net heat of combustion of these fuels are as follows:

Hydrogen content and heat of combustion of four fuels.

Kind of fuel.	Hydrogen.	Total heat of combustion.	Net heat of combustion.	Heat lost in water vapor at 20° C.
	Per cent.	*B. t. u.*	*B. t. u.*	*Per cent.*
Bituminous coal	5.18	13,560	13,075	3.6
Anthracite	2.50	12,780	12,545	1.8
Petroleum	12.75	18,540	17,345	6.4
Coke	.30	12,500	12,470	0.2

Obviously a comparison of coke and petroleum on the basis of total heats of combustion would be unfair to the coke; practically all of its heat is available, whereas 6.4 per cent of the total heat of the petroleum remains in uncondensed water vapor.

ESTIMATION OF HYDROGEN FROM VOLATILE MATTER.

Probably the net heat of combustion would be used in fuel calculations more often if the hydrogen content could be estimated without an expensive ultimate analysis; and, as 1 per cent hydrogen corresponds to a correction of only 94 B. t. u. it seems probable that the hydrogen in coal can be estimated accurately enough from the percentage of volatile matter. The lowest percentage of hydrogen is found in anthracites which contain 3 to 10 per cent volatile matter; the higher percentages of hydrogen are found in lignites and coals, especially cannel coals, which produce large percentages of volatile matter.

A comparison of the analyses of coals of various ranks shows a rough relation between the increase of hydrogen and that of volatile matter. The obvious method of determining this relation and the deviation that may be expected in individual samples is to plot the values for hydrogen and volatile matter for a large number of coals of various rank, and then note whether a smooth curve can be drawn through these points. The deviation of these points from the curve will show the probable error for hydrogen values calculated from the volatile matter. The first use of this method of estimating the percentage of hydrogen in coal from the percentage of volatile matter was in 1908 by Marks.[a] He constructed a hydrogen-volatile matter curve from 240 ultimate analyses of different coals tested at the Government fuel testing plant at St. Louis.

The curves given in this paper have been determined in a similar manner from 2,000 ultimate analyses[b] made by the Bureau of Mines of coals from various parts of the United States.

[a] Marks, L. S., The ultimate analysis of coal; Power, vol. 29, 1908, pp. 928–931.

[b] Lord, N. W., and others, Analyses of coals in the United States, July 1, 1904, to June 30, 1910, Bull. 22, Bureau of Mines, 1913, 1129 pp.; Fieldner, A. C., and others, Analyses of mine and car samples of coal collected in the fiscal years 1911 to 1913, Bull. 85, Bureau of Mines, 1914, 444 pp.

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CONSTRUCTING THE CURVES SHOWING RATIO OF HYDROGEN TO VOLATILE MATTER.

As the moisture content and ash content of a given type of coal are to some degree accidental and variable, all the analyses used in establishing the curves were computed to a moisture and ash free basis, thus obtaining the approximate percentages of volatile matter and hydrogen in the actual coal substance. These values for some 2,000 coals and lignites from practically all parts of the United States were tentatively plotted on a single sheet. An inspection of the grouping of the points obtained for the ratio of hydrogen to volatile matter suggested that curves might be obtained showing somewhat less deviation of extreme points if the analyses were subdivided into several groups according to the calorific value on the moisture and ash free basis; this would further subdivide those coals and lignites having different ratios of hydrogen to volatile matter.

INCREASE OF MOISTURE AND ASH FREE CALORIFIC VALUE WITH THE RANK OF THE COAL.

White[a] has shown that the rank or grade of a coal increases as the percentage of oxygen decreases, and it can likewise be shown that the moisture and ash free calorific value of lignite and bituminous coal increases with the rank of the coal. In the 2,000 analyses used for constructing the curves given herein it was found that the moisture and ash free calorific value varied from about 10,000 B. t. u. for low rank and somewhat weathered lignite to about 16,000 B. t. u. for the best semibituminous coal, such as Pocahontas and New River. Between these extremes are the various coals and lignites having moisture and ash free calorific values substantially as follows:

Calorific values of moisture and ash free coals.

	Calorific value, B. t. u.
Weathered lignite and subbituminous coal	9,400 to 12,000
Unweathered lignite and subbituminous coal	12,000 to 13,800
Low-rank western bituminous coal, verging on subbituminous	13,300 to 14,000
High-moisture bituminous coal, such as occurs in Indiana, Illinois, Missouri, Washington, and other Western States	14,000 to 14,800
Medium-rank bituminous coal, such as occurs in Ohio, Tennessee, Kentucky, Illinois, and some of the Western States	14,300 to 15,000
High-rank bituminous coal, such as occurs in Pennsylvania, West Virginia, and Kentucky	14,800 to 15,700
Semianthracite and semibituminous coal	15,300 to 16,000
Best semibituminous coal, such as the Pocahontas and New River of West Virginia	15,500 to 15,900
Anthracite	14,800 to 15,500

[a] White, David, The effect of oxygen in coal; U. S. Geol. Survey Bull. 382, 1909, 74 pp.; Bull. 29, Bureau of Mines, 1911, 80 pp.

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CLASSIFICATION OF COAL AND LIGNITE ACCORDING TO MOISTURE AND ASH FREE CALORIFIC VALUE.

In order to determine the proper number of subdivisions, according to moisture and ash free calorific value, for plotting the hydrogen and volatile matter curves, an arbitrary division was made for each increase of 500 B. t. u. In this manner the 2,000 analyses were plotted in nine divisions and the curve for hydrogen and volatile matter was drawn for each division. Comparison of the resulting curves showed that these nine divisions could be combined into four divisions without increasing materially the deviation of the individual points from the average curves. These four divisions are given in figures 1 to 4, inclusive.

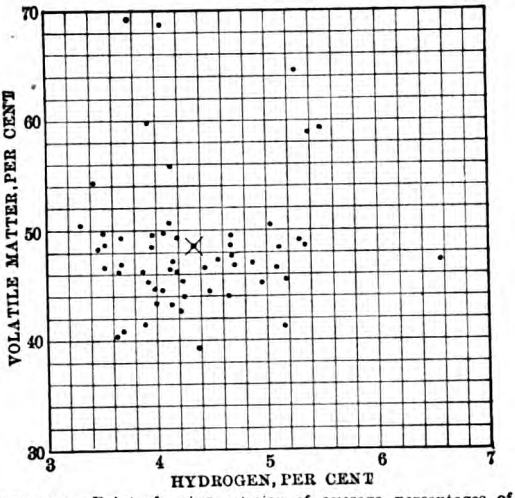

FIGURE 1.—Point showing relation of average percentages of hydrogen and volatile matter of coals and lignites having calorific values of less than 12,000 B. t. u., moisture and ash free.

In figure 1 an average value, indicated by a cross, was made for the hydrogen content and the volatile matter content for all of the coals in this division. For the curves shown in figures 2, 3, and 4, the coals were grouped for each whole per cent of volatile matter, and average values for hydrogen and volatile matter were made for each group. These average values, indicated by cross marks, were used in plotting the curves.

Figure 1 includes all analyses in which the moisture and ash free calorific values are less than 12,000 B. t. u.; figure 2 includes calorific values between 12,000 and 12,499 B. t. u.; figure 3 includes calorific values between 12,500 and 14,499 B. t. u.; and figure 4 includes all calorific values above 14,499 B. t. u. Each point in figures 1 and 2 represents a single analysis.

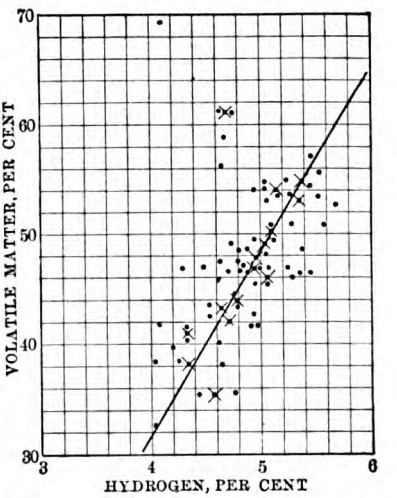

FIGURE 2.—Curve showing relation between the percentages of hydrogen and volatile matter of coals and lignites having calorific values of 12,000 to 12,499 B. t. u., inclusive, moisture and ash free.

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In figures 3 and 4 it was not possible to show the large number of available analyses by individual points in the more densely dotted regions near the curve; however, all the analyses that did not fall in this region are represented by individual points, so that the maximum deviations from the curves are clearly represented.

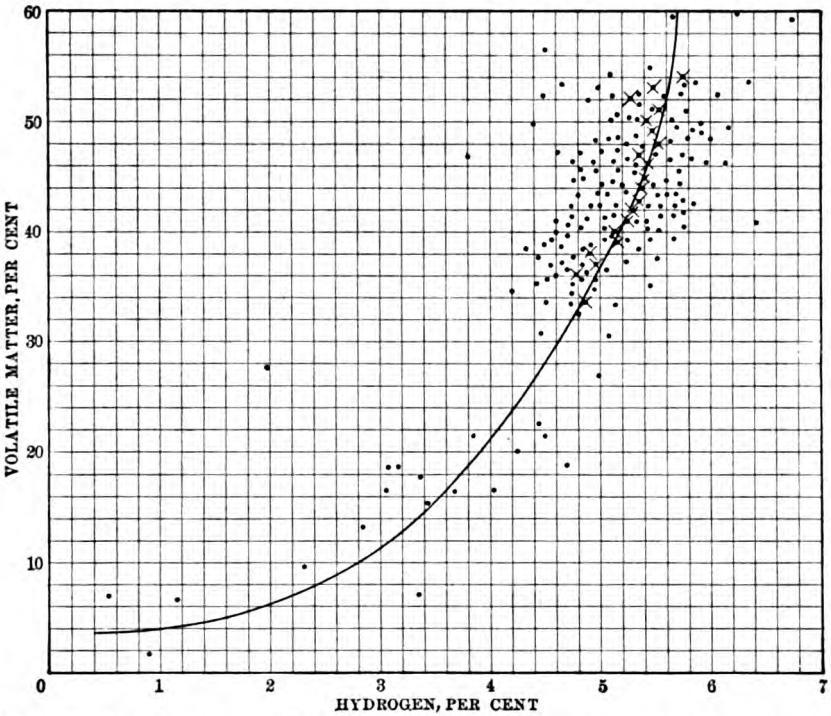

FIGURE 3.—Curve showing relation between the percentages of hydrogen and volatile matter of coals and lignites having calorific values of 12,500 to 14,499 B. t. u., inclusive, moisture and ash free.

USE OF THE CURVES FOR ESTIMATING HYDROGEN.

The approximate percentage of hydrogen in any coal or lignite may be estimated from the proximate analysis and calorimetric determination in the following manner:

(1) Compute the moisture and ash free B. t. u. and volatile matter by the following formulas:

$$\text{B. t. u.} \times \frac{100}{100-(\text{per cent moisture}+\text{per cent ash})} = \text{moisture and ash free B. t. u.}$$

$$\text{Per cent volatile matter} \times \frac{100}{100-(\text{per cent moisture}+\text{per cent ash})} = \text{moisture and ash free volatile matter.}$$

(2) Refer to the appropriate curve for the B. t. u. obtained, and read the percentage of hydrogen corresponding to the given moisture and ash free volatile matter.

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(3) Compute the moisture and ash-free hydrogen so obtained to the condition in which the remainder of the analysis is stated by the following formula:

$$\text{Per cent moisture and ash free hydrogen} \times \frac{100-(\text{per cent moisture}+\text{per cent ash})}{100} = \text{per cent hydrogen in coal as received.}$$

PROBABLE ERROR IN COMPUTED HYDROGEN VALUE.

The probable error of the result calculated from the amount of volatile matter varies somewhat in the different groups, as may be

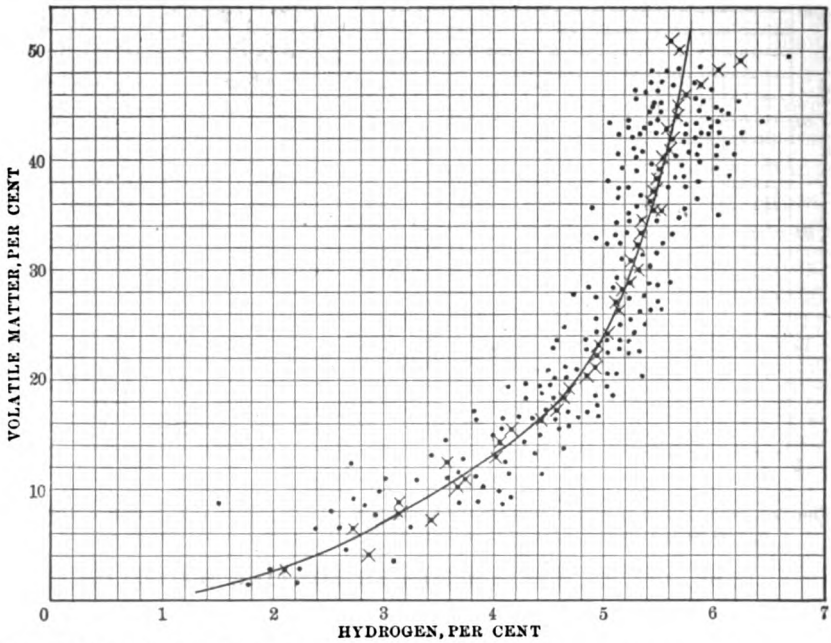

FIGURE 4.—Curve showing relation between the percentages of hydrogen and volatile matter of coals having calorific values of 14,500 B. t. u. and higher, moisture and ash free.

seen from an inspection of the four curves. Figure 1, which represents lignites and subbituminous coals that may have been altered by weathering, shows little relation between the percentages of hydrogen and volatile matter. The deviation of the points from the average point with respect to hydrogen will in most instances be within ± 1 per cent.

Figure 2 shows a fairly close relation between hydrogen and volatile matter, there being only four analyses in this group in which the hydrogen content deviates more than 0.8 per cent from the curve.

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Figure 3 represents 700 analyses, of which only 20 deviate from the curve by more than 0.6 per cent hydrogen.

Figure 4 represents 1,200 analyses, of which only 10 deviate from the curve by more than 0.6 per cent hydrogen.

CONCLUSIONS.

By the use of curves constructed from 2,000 analyses the hydrogen content of bituminous coal, semibituminous coal, and anthracite may be estimated from the volatile matter to within 0.6 per cent. For subbituminous coal and lignite the limits of deviation should be extended to 0.8 per cent, and if the coals are weathered the error may approach 1 per cent. The corresponding errors produced in the reduction of "total" to "net" heat of combustion are shown in the computations below, the values obtained being the errors in net heat of combustion through the errors in computed hydrogen:

$$\frac{1040\times9\times0.6}{100}=56 \text{ B. t. u.}$$

$$\frac{1040\times9\times0.8}{100}=75 \text{ B. t. u.}$$

$$\frac{1040\times9\times1.0}{100}=94 \text{ B. t. u.}$$

In most coals the error in the net heat of combustion calculated in the above manner will not exceed 0.5 per cent, which is no larger than the errors incurred in sampling coal.

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BULLETIN 85. Analyses of mine and car samples of coal collected in the fiscal years 1911 to 1913, by A. C. Fieldner, H. I. Smith, A. H. Fay, and Samuel Sanford. 1914. 444 pp., 2 figs.

BULLETIN 119. Analyses of coals purchased by the Government during the fiscal years 1908–1915, by G. S. Pope. 1916. 118 pp.

BULLETIN 136. Deterioration in the heating value of coal during storage, by H. C. Porter and F. K. Ovitz. 1917. 38 pp., 7 pls.

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TECHNICAL PAPER 8. Methods of analyzing coal and coke, by F. M. Stanton and A. C. Fieldner. 1913. 42 pp., 12 figs.

TECHNICAL PAPER 16. Deterioration and spontaneous heating of coal in storage, a preliminary report, by H. C. Porter and F. K. Ovitz. 1912. 14 pp.

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TECHNICAL PAPER 64. The determination of nitrogen in coal, a comparison of various modifications of the Kjeldahl method with the Dumas method, by A. C. Fieldner and C. A. Taylor. 1915. 25 pp., 5 figs.

TECHNICAL PAPER 76. Notes on the sampling and analysis of coal, by A. C. Fieldner. 1914. 59 pp., 6 figs.

TECHNICAL PAPER 98. Effect of low-temperature oxidation on the hydrogen in coal and the change of weight of coal in drying, by S. H. Katz and H. C. Porter. 1917. 16 pp., 2 figs.

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TECHNICAL PAPER 133. Directions for sampling coal for shipment or delivery, by G. S. Pope. 1917. 15 pp., 1 pl.

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TECHNICAL PAPER 140. The primary volatile products of the carbonization of coal; a sequel to Bulletin 1, The volatile matter of coal, by G. B. Taylor and H. C. Porter. 1916. 59 pp., 1 pl., 25 figs.

TECHNICAL PAPER 148. The determination of moisture in coke, by A. C. Fieldner and W. A. Selvig. 1917. 13 pp.

TECHNICAL PAPER 170. The diffusion of oxygen through stored coal, by S. H. Katz. 1917. 49 pp., 1 pl., 27 figs.

TECHNICAL PAPER 172. Effects of moisture on the spontaneous heating of stored coal, by S. H. Katz and H. C. Porter. 1917. 25 pp., 1 pl., 8 figs.

PUBLICATIONS THAT MAY BE OBTAINED ONLY THROUGH THE SUPERINTENDENT OF DOCUMENTS.

BULLETIN 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitz. 1910. 56 pp., 1 pl., 9 figs. 10 cents.

BULLETIN 11. The purchase of coal by the Government under specifications, with analyses of coal delivered for the fiscal year 1908–9, by G. S. Pope. 80 pp. 10 cents.

BULLETIN 22. Analyses of coals in the United States, with descriptions of mine and field samples collected between July 1, 1904, and June 30, 1910, by N. W. Lord, with chapters by J. A. Holmes, F. M. Stanton, A. C. Fieldner, and Samuel Sanford. 1912. Part I, Analyses, pp. 1–321; Part II, Descriptions of samples, pp. 321–1129. 85 cents.

BULLETIN 29. The effect of oxygen in coal, by David White. 80 pp., 3 pls. 20 cents.

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TECHNICAL PAPER 65. A study of the oxidation of coal, by H. C. Porter. 1914. 30 pp., 12 figs. 5 cents.

TECHNICAL PAPER 93. Graphic studies of ultimate analyses of coals, by O. C. Ralston, with a preface by H. C. Porter. 1915. 41 pp., 3 pls., 6 figs. 10 cents.

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